DOCUMENT RESUME

ED 135 585 SE 021 576

AUTHOR	Zdravkovich, V.
TITLE	Organic Chemistry Self Instructional Package 5: Alkanes Preparations and Reactions.
INSTITUTION	Prince George's Community Coll., Largo, Md.
PUB DATE	76
NOTE	50p.; For related Packages 1-17, see SE 021 572-588; Not available in hard copy due to copyright restrictions
AVAILABLE FROM	Prince George's Community College Bookstore, Largo, Maryland 20870 ($17.00 a set, $1.00 ea.)
EDRS PRICE	MF-$0.83 Plus Postage. HC Not Available from EDRS.
DESCRIPTORS	*Autoinstructional Aids; *Chemistry; *College Science; Higher Education; *Independent Study; Individualized Instruction; Individualized Programs; *Organic Chemistry; Science Education; Self Help Programs
IDENTIFIERS	Alkanes; Prince Georges Community College

ABSTRACT

This booklet, one of a series of 17 developed at Prince George's Community College, Largo, Maryland, provides an individualized, self-paced undergraduate organic chemistry instruction module designed to augment any course in organic chemistry but particularly those taught using the text "Organic Chemistry" by Morrison and Boyd. The entire series of modules covers the first 13 chapters of the Morrison-Boyd text in great detail. Each module has been provided with from one to three audiotapes, available from Prince George's Community College, to provide students additional explanations of particular concepts. Each module includes a self-evaluation exercise, a reference guide, worksheets to be completed with the audiotapes, answer sheets for the worksheets, a progress evaluation, an answer sheet for the progress evaluation, an answer sheet for the self-evaluation exercise, an introduction to the topic covered by the module, and student performance objectives for the module. The topic of this module is alkanes-preparations. (SL)

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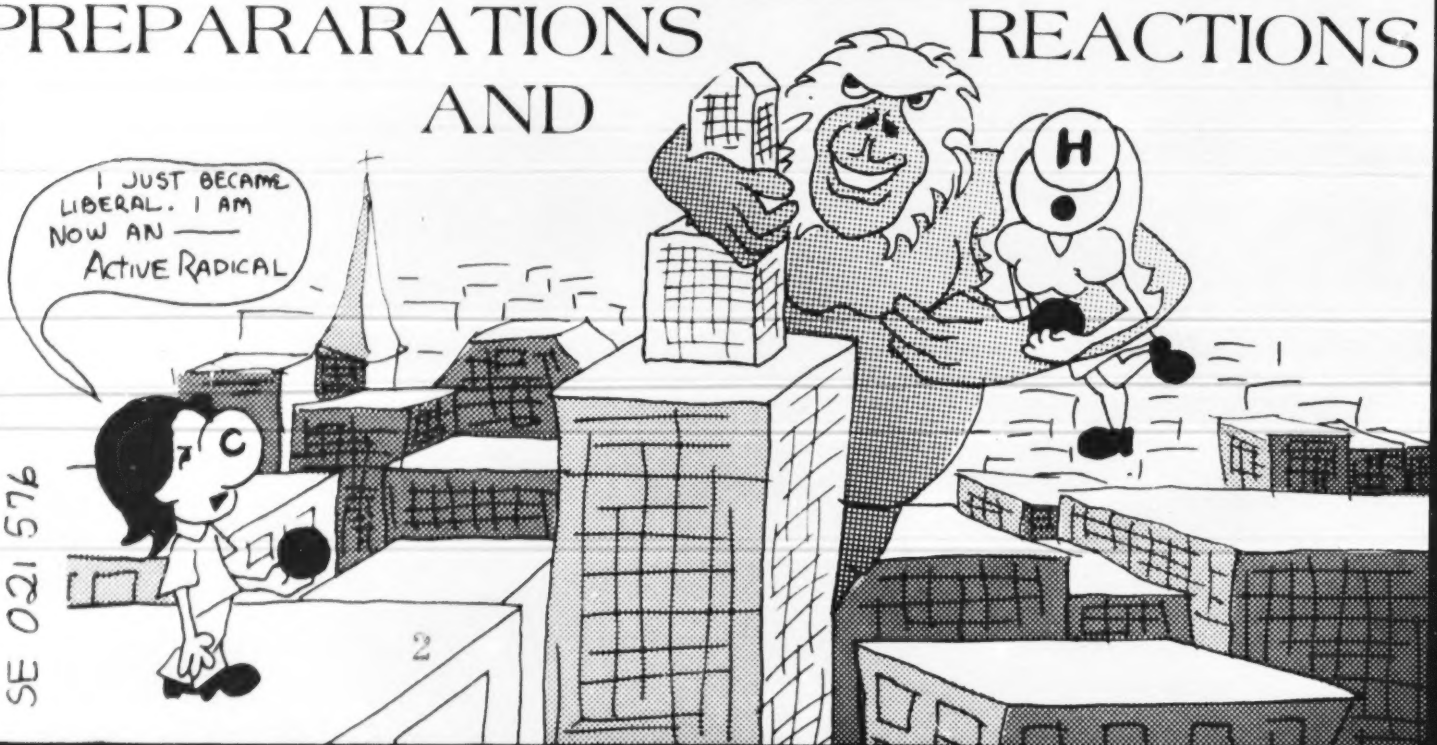
ALKANES
PREPARARATIONS AND REACTIONS



SE 021 576

Self Instructional Sequence in

ORGANIC CHEMISTRY

"Copr.," V. Zdravkovich 1976

ALKANES - PREPARATIONS

For 1912, the Nobel Prize was awarded to Victor Grignard (1871-1935) "For the discovery of the so-called Grignard reagent, which has greatly helped in the development of organic chemistry during these last years."

DESCRIPTION OF THE PRIZE-WINNING WORK*

"The preparation of the organo-magnesium ethers is, in general, extremely simple. The apparatus is just a round-bottomed flask connected with a good ascending condenser and with a dropping funnel with stopcock, but it is indispensable that everything be absolutely dry.

"One atomic weight of magnesium, in the form of fine filings, is placed into the flask. On the other hand, one molecular weight of the halogenated hydrocarbon to be used--for example, methyl iodide-is dissolved in an almost equal volume of perfectly dry ether which was kept over sodium. Of this mixture, 25-30 c.c. are added to the magnesium. A lively reaction begins after a very short time. Then, 250-300 c.c. of ether are added, and the reaction is kept going by addition of the rest of the reaction mixture drop by drop. The reaction is completed by short heating, if necessary. Under these conditions the magnesium disappears completely. In general, a clear or slightly colored solution is obtained, in which, however, very fine particles of iron, an impurity in the magnesium, produce a momentary haze of slate color.

"The compound, prepared as just indicated, shows all the characteristics of organo-metallic compounds; it changes rapidly in air, absorbs oxygen and carbon dioxide, is decomposed violently by water, and reacts strongly with almost all functional groups. These operations can usually be carried out without any change in the apparatus. It suffices to add, through the dropping funnel, the antagonistic compound dissolved in a convenient quantity of water-free ether. Thus, either a solution or an oily or crystalline separation is obtained, and the reaction is completed, if necessary, by a more or less prolonged heating. After that, all that remains to be done is to hydrolyze the compound."

*Translated from "Le magnesium en chimie organique," Bulletin de la Societe Chimique de France, Vol. XIII (1913), p. 1.

Self Instructional Package No. 5
Form A - Set of Objectives

DEFINITIONS -

The student will be able to define and illustrate with appropriate examples where applicable the following terms: GRIGNARD compound, GRIGNARD synthesis, WURTZ synthesis, ORIENTATION, REACTIVITY, SELECTIVITY, CRACKING, PYROLYSIS, HYDROCRACKING, STEAM CRACKING, KNOCKING, COMBUSTION, HEAT OF COMBUSTION.

PREPARATIONS -

The student will be able to write the chemical reactions for the following preparations: Grignard synthesis, Wurtz synthesis, Lithium-Copper synthesis and synthesis using Zinc and Acid.

The student will be able to determine the reagents required for the synthesis of a given alkane from a given reactant. From the given reagents and the product desired, the student will be able to identify the reactant required for the synthesis.

The student will be able to explain why the Grignard synthesis is a two-step synthesis and why it requires dry apparatus.

REACTIONS -

The student will be able to write the balanced reactions for combustion and halogenation of different alkanes.

The student will be able to write the step by step mechanisms for the halogenation of alkane reactions.

The student will be able to predict the orientation in the halogenation of alkane reaction and consequently identify the intermediates and the major product.

The student will be able to compare different alkanes and different halogens with respect to their reactivity.

The student will be able to compare different halogens with respect to their selectivity.

The student will be able to calculate the percentage composition of the mixture of the products obtained in the chlorination or the bromination of simpler alkanes (not more than 5 C atoms).

MULTI-STEP SYNTHETIC SCHEMES -

The student will be able to devise multi-step synthesis schemes for the synthesis of different alkanes from a given reactant.

The student will be able to identify all the reagents in a given multi-step synthetic scheme.

The student will be able to identify the intermediate compounds formed in a multi-step synthetic scheme.

Self Instructional Package No. 5
Form B - Self Evaluation Exercise

ALKANES - PREPARATIONS AND REACTIONS

1. The reagents which can be used to prepare BUTANE from 2-BROMO BUTANE are:

   a) SODIUM

   b) ZINC, ACID

   c) Li, CuBr, METHYL CHLORIDE

   d) MAGNESIUM, ETHER, WATER

2. The following statements about the Grignard Synthesis are true:

   a) Grignard compound will react with water or alcohol.

   b) Grignard synthesis is a two step synthesis.

   c) The apparatus used in the Grignard synthesis must be dry.

   d) Water, magnesium and ether are added to the reactant in the first step.

3. Identify the correct statements below:

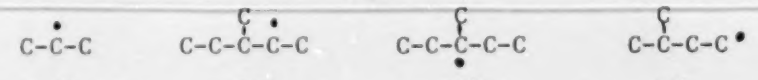
   a) Best results in Wurtz synthesis are obtained with primary alkyl halides.

   b) Wurtz synthesis is useful only for the synthesis of symmetrical alkanes.

   c) Lithium dialkyl copper compounds gives best result in the reaction with tertiary alkyl halides.

   d) The function of ether in Grignard synthesis is to slow down the reaction.

4. In a series of free radicals listed below, identify the one with maximum stability and the one with minimum stability.



I II III IV

Maximum Stability	Minimum Stability
a) I	a) IV
b) II	b) III
c) III	c) IV
d) IV	d) III

5. Identify the correct statements about the halogenation of alkane reaction:

   a) Bromine is more reactive than chlorine.

   b) Bromine is more selective than chlorine.

   c) Bromination of isobutane will produce larger percentage of the major product than chlorination.

   d) Bromine reacts faster than chlorine.

6. The major product obtained in the bromination of 3-methyl pentane is:

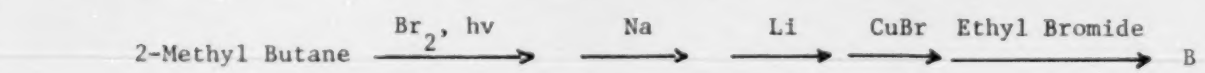
   a) 1-Bromo-3-Methyl Pentane

   b) 2-Bromo-3-Methyl Pentane

   c) 3-Bromo-3-Methyl Pentane

   d) 2-Bromo-2-Methyl Pentane

7. Identify compound B produced in the reaction sequence below:



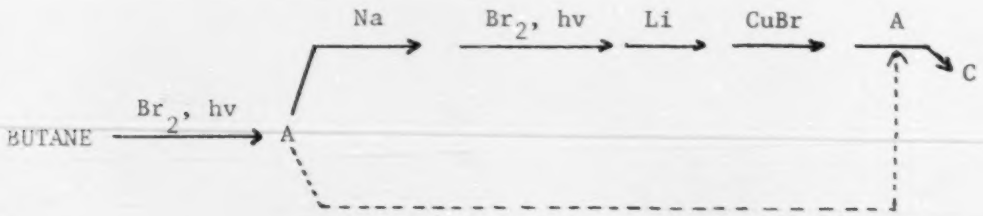
   a) 3,3,4,4,5-Pentamethyl Heptane

   b) 3,6-Dimethyl-3-Ethyl-Octane

   c) 3,3,4,4-Tetramethyl Octane

   d) 3,6-Dimethyl Decane

8. Identify compound C formed in the reaction sequence below:



a) 3,4,7-Trimethyl Nonane

b) 3,4,5-Trimethyl-4-Ethyl Heptane

c) 3,4-Dimethyl Decane

d) 3,4-Dimethyl-4-Ethyl Octane

9. The reagents required for the laboratory synthesis of 3-Methyl Pentane from Ethyl Bromide are:

a) SODIUM, Br_2, Light; Li; CuBr; PROPYL BROMIDE

b) ZINC, Br_2, Light; Li; CuBr; ETHYL BROMIDE

c) SODIUM

d) SODIUM, Br_2, Light; Li; CuBr; ETHYL BROMIDE

10. The reagents that could be used for the laboratory synthesis of 2,3-Dimethyl Butane from Propane are:

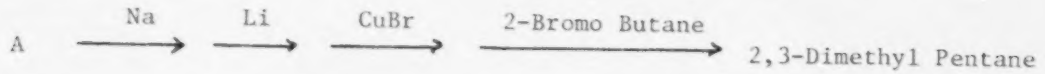
a) BROMINE, Light; SODIUM

b) BROMINE, Light; ZINC, ACID

c) BROMINE, Light; Li; CuBr; ISOPROPYL BROMIDE

d) BROMINE, Light; Li; CuBr; PROPYL BROMIDE

11. The reactant A which should be used in the synthesis below is:



a) Ethyl Bromide

b) Propyl Bromide

c) Propane

d) Isopropyl Bromide

12. Reaction of an alkane with heat and excess oxygen will yield:

a) Alkenes

b) carbon dioxide, water

c) smaller alkanes

d) carbon dioxide, water, heat

13. Cracking of alkanes can be defined as:

a) pyrolysis of alkanes

b) decomposition of larger alkanes by the action of heat

c) reaction of alkanes with excess oxygen

d) reaction of alkanes with steam

14. Circle the correct statements below:

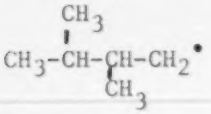
a) Hydrocracking is the cracking of alkanes in the presence of oxygen.

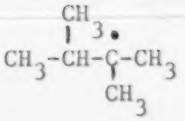
b) Octane number indicates the relative anti-knock tendency of the fuel.

c) "Iso-octane" has a low octane number.

d) Tetraethyllead is added to the gasoline to increase the amount of "iso-octane".

15. The intermediate species in the chlorination of 2,3-dimethyl butane are:

a) 

b) 

c) $Br^{\bullet}$

d) Heat

Self Instructional Package No. 5
Form C - Reference Guide

ALKANES - PREPARATIONS AND REACTIONS

The Reference Guide should be used in conjunction with Form B or the Self Evaluation Exercise. The references give the correlation between the questions in Form B and the available material in the textbook and in the form of tapes.

Questions 1,2,3,9,10,11	Chapter 3, Section 15,16,17	Morrison & Boyd Organic Chemistry
Question 4	Chapter 3, Section 24	
Questions 5,6	Chapter 3, Sections 21,22,27,28	
Question 15	Chapter 3, Section 20,21	
Question 12	Chapter 3, Section 30	
Questions 13,14	Chapter 3, Sections 30,31	

In addition to the above-mentioned sections of Chapter 3 in your textbook, additional explanations and examples to be used for Questions 1,2,3,7,8,9, 10,11, can be found in TAPE 1 - with the accompanying worksheet and answer sheet titled, Alkanes-Preparations.

For Questions 4,5,6,7,8,9,15, additional explanation and examples are provided in TAPE 2 - with the accompanying worksheet and answer sheet titled, Alkanes-Reactions.

When a king asked Euclid, whether he could not explain his art to him in a more compendious manner, he was answered, that there was no royal way to geometry. Other things may be seized by might, or purchased with money; but knowledge is to be gained only by study, and study to be prosecuted only in retirement.

---Johnson

Self Instructional Package No. 5
Tape 1 - Worksheet

ALKANES - PREPARATION

I. Hydrogenation of Alkenes

$$C_nH_{2n} + H_2 \xrightarrow{Pt, Pd \text{ or } Ni} C_nH_{2n+2}$$

Alkene Alkane

II. Direct Reduction of Alkyl Halides

Alkyl Halide RX (R = Alkyl group X = Halogen Atom)

$$RX + Zn + H^+ \longrightarrow RH + Zn^{++} + X^-$$

Or

$$RX \xrightarrow{Zn, \text{ Acid}} RH$$

III. Grignard Reaction - Indirect Reduction of Alkyl Halides

$$RX + Mg \xrightarrow{\text{Ether}} RMgX \xrightarrow{HA} RH + Mg(A)\,X$$

RX: Alkyl Halide; RMgX: Organo-magnesium Halide, Grignard Compound; RH: Alkane

Or

$$RX \xrightarrow[\text{Ether}]{Mg} RMgX \xrightarrow[NH_3]{H_2O \text{ or } ROH \text{ or}} RH$$

Step 1 Step 2

SIP #5 - Tapel Worksheet

IV. Wurtz Reaction

$$2RX + 2\,Na \longrightarrow R\text{-}R + 2NaX$$

Alkyl Halide — Alkane

Or

$$RX \xrightarrow{Na} R\text{-}R$$

V. $$RX + 2Li \longrightarrow RLi + LiX$$

$$2\,RLi + CuX \longrightarrow R_2CuLi + LiX$$

$$R_2LiCu + R^1X \longrightarrow R\text{-}R^1 + RCu + LiX$$

Or (abbreviated version)

$$RX \xrightarrow{Li} RLi \xrightarrow{CuX} R\,LiCu \xrightarrow{R^1X} R\text{-}R^1$$

Alkyl Halide	Intermediate I Alkyl Lithium	Intermediate II Lithium Dialkyl Copper Compound	Alkane

Example 1. Grignard Reaction

Step 1.

$$RX + Mg \xrightarrow[\text{anhydrous}]{\text{ether}} R^{\delta-} \text{ (polar bond) } Mg^{\delta+} \text{ (ionic bond) } X^-$$

Grignard Reagent ($R^{\delta-}$ has a considerable carbanion character)

Step 2.

$$R\,Mg\,X + HOH \longrightarrow R\text{-}H + Mg(OH)X$$

Salt of weaker acid — stronger acid — weaker acid (Alkane) — Magnesium Hydroxy Halide

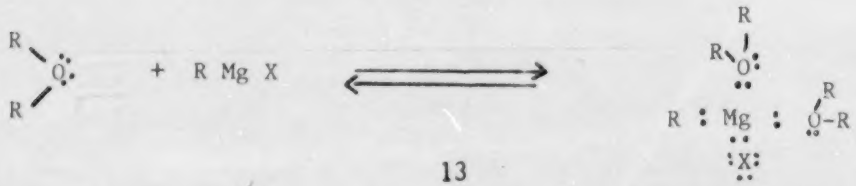
$$R\,Mg\,X + H\,NH_2 \longrightarrow R\text{-}H + Mg(NH_2)X$$

stronger acid (Ammonia) — Magnesium Amino Halide

$$R\,Mg\,X + HOR \longrightarrow R\text{-}H + Mg(OR)X$$

stronger acid (Alcohol) — Magnesium Alcoxy Halide

Solvation of Grignard Reagent by Diethyl Ether



Self Instructional Package No. 5
Tape 1 - Worksheet

Assignment No. 1

Write the reactions for the preparation of 3-methyl pentane from 1-chloro-3-methyl pentane

Assignment No. 2

Inert Irma was asked to describe the preparation of isobutane from isobutylbromide. Her answer is given below.

Identify all the mistakes and correct her answer.

I. Reaction with zinc and acid

$$CH_3\ CH\ (CH_3)\ CH_2\ Br \xrightarrow{Zn} CH_3\ CH\ (CH_3)_2$$

II. Grignard Reaction

$$CH_3\ CH\ (CH_3)\ CH_2\ Br \xrightarrow{H_2O} \xrightarrow{Mg\ Ether} CH_3\ CH\ (CH_3)_2$$

Assignment No. 3

Identify the reagents in each one of the preparations listed below.

2-Bromo Butane ⟶ 3,4-Dimethyl Hexane

2-Bromo Butane ⟶ Butane

1-Chloro-2-Methyl Butane ⟶ 3,6-Dimethyl Octane

SIP #5 - Tape 1 Worksheet

Assignment No. 4

Confused Clyde was asked to identify the reactants in the preparation of a number of alkanes. His answer is given below. Make all the necessary corrections.

a. Isopropyl Bromide $\xrightarrow{\text{Zn, Acid}}$ 2,3-Dimethyl Butane

b. 2-Bromo Butane $\xrightarrow{\text{Na}}$ 2,3-Dimethyl Butane

c. 2-Bromo Butane $\xrightarrow[\text{Ether}]{\text{Mg}}$ $\xrightarrow{H_2O}$ Butane

Example 2. Wurtz Synthesis

$$RX \xrightarrow{Na} R\text{-}R$$

Alkyl Halide → Alkane

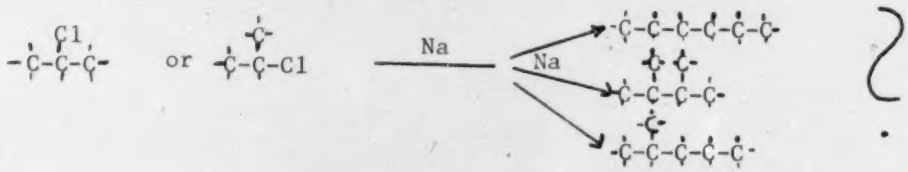
$$R\text{-}X + 2Na \longrightarrow R^{-}\text{-}Na^{+} + NaX$$

$$R{:}^{-}\ Na^{+} + R{:}X \longrightarrow R\text{-}R + NaX$$

Example 3.

$$CH_3Cl \xrightarrow{Na} CH_3 - CH_3$$

$$CH_3\text{-}CH_2\ Br \xrightarrow{Na} CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

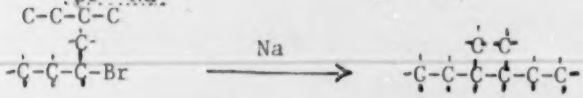


Example 4.

a. $R\text{-}X + X\text{-}R \longrightarrow R\text{-}R + NaX$ (Na, Na)

Plane of Symmetry

b.

Or 

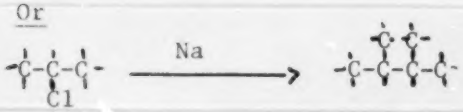
Plane of Symmetry

SIP #5 - Tape 1 Worksheet

Example 4. (continued)

c.

Or



Assignment No. 5

Identify i.e. draw the structures and name the products in the following reactions:

2-Bromo Pentane $\xrightarrow{Na}$

2-Bromo-3-Methyl Butane $\xrightarrow{Na}$

1-Chloro-3-Methyl Pentane $\xrightarrow{Na}$

n-Butyl Chloride $\xrightarrow{Na}$

Assignment No. 6

Identify i.e. draw the structure and name the reactants in the reactions below.

$\xrightarrow{Na}$ 2,3-Dimethyl Butane

$\xrightarrow{Na}$ Decane

$\xrightarrow{Na}$ 2,3,6,7-Dimethyl Octane

$\xrightarrow{Na}$ 3,4-Diethyl Hexane

Assignment No. 7

From the list of products supplied below, identify the ones which correspond to the given reactions.

1-Bromo -4-Methyl Hexane $\xrightarrow{Zn,acid}$

2-Bromo Hexane $\xrightarrow{Na}$

3-Bromo Hexane $\xrightarrow{Na}$

2-Bromo-3-Methyl Pentane $\xrightarrow{Na}$

3-Chloro-2-Methyl Pentane $\xrightarrow{Mg,\ Ether}$ $\xrightarrow{H_2O}$

17

SIP #5 - Tape 1 Worksheet

Assignment No. 7 (continued)

Products:

(1) 3,4,5,6-Tetramethyl Octane

(2) 4,5-Diethyl Octane

(3) 2-Methyl Pentane

(4) 3-Methyl Hexane

(5) 5.6-Dimethyl Decane

Assignment No. 8

Forgetful Frieda was asked to identify the reactants and the reagents in a number of synthesis. She has done so but forgot to identify them with the correct product. Match the reactants and the reagents with the correct products.

Reactants	Products	Reagents
(1) 2-Bromo-4-Methyl Hexane	(1) 3,4,-Diethyl Hexane	
(2) 2-Chloro-3Ethyl Pentane	(2) 2,5-Dimethyl Hexane	Na
(3) 3-Bromo Pentane	(3) 2,5-Dimethyl Heptane	or
(4) 3-Bromo-4-Ethyl Hexane	(4) 4,5-Dimethyl-3,6-Diethyl Octane	Mg, Ether H_2O
(5) Isobutyl Chloride	(5) 3-Methyl Hexane	or
(6) 1-Bromo-2,5-Dimethyl Heptane	(6) 3-Ethyl Hexane	Zn, Acid

Assignment No. 9

Identify (draw the structures and name) all the products obtained in a reaction of a mixture of aklylhalides: idopropyl chloride and n-butyl chloride with sodium.

Assignment No. 10

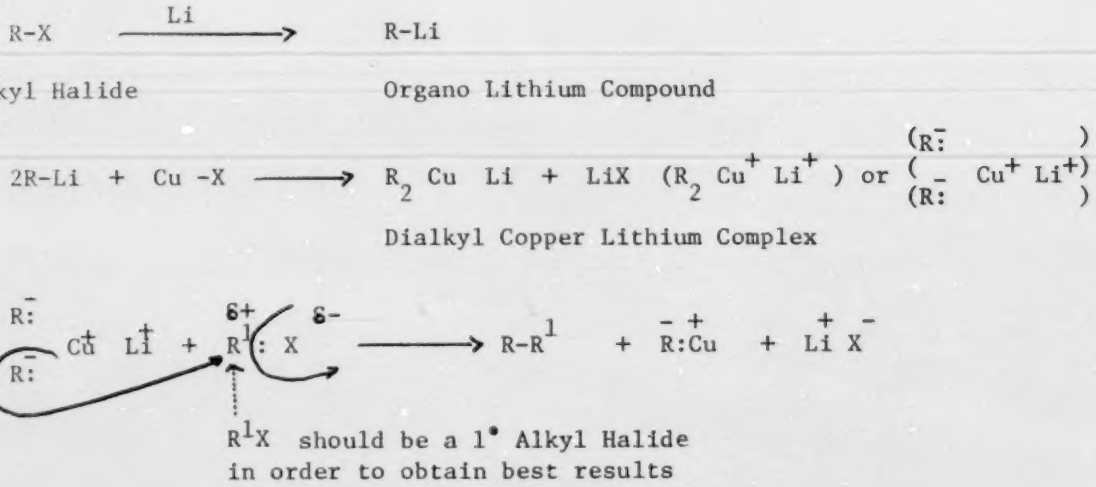
When a mixture of two alkyl halides reacted with sodium, the following products were obtained. Identify the original reactants.

products: 2,4-dimethyl hexane ; 3,4 dimethyl hexane
2,5-dimethyl hexane

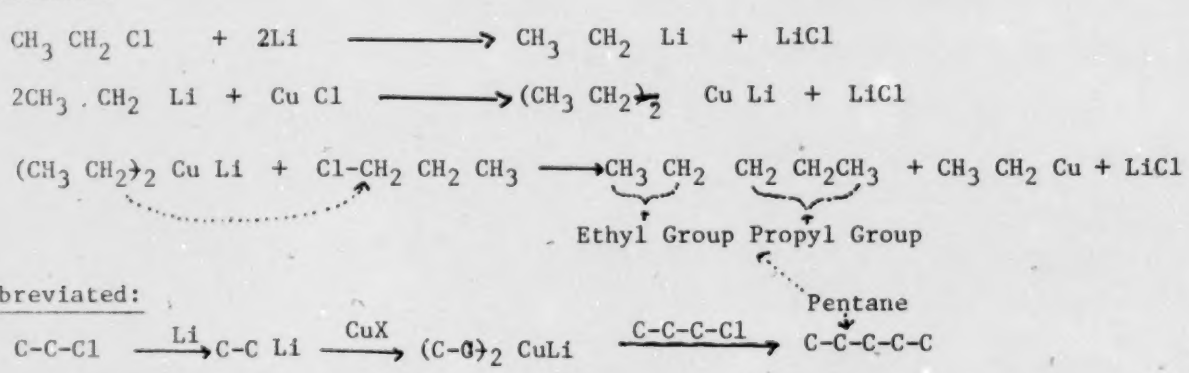
SIP #5 - Tape 1 Worksheet

Assignment No. 10 (continued)

Example 5. - Copper Lithium Reaction

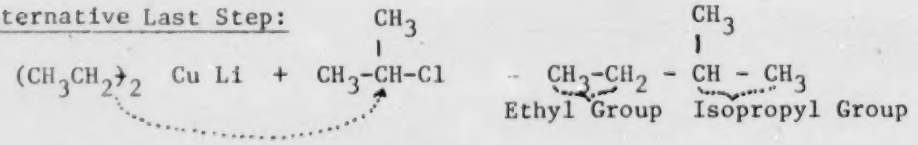

R-X
Li
R-Li
Alkyl Halide
Organo Lithium Compound
2R-Li + Cu -X
R2 Cu Li + LiX (R2 Cu+ Li+) or (R: Cu+ Li+) (R:)
Dialkyl Copper Lithium Complex
R: Cu Li + R1 : X
R-R1 + R:Cu + Li X
R1X should be a 1° Alkyl Halide
in order to obtain best results

Example 6.

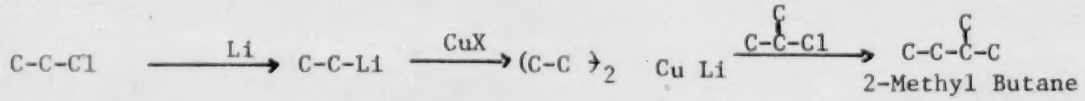

CH3 CH2 Cl + 2Li
CH3 CH2 Li + LiCl
2CH3 CH2 Li + Cu Cl
(CH3 CH2)2 Cu Li + LiCl
(CH3 CH2)2 Cu Li + Cl-CH2 CH2 CH3
CH3 CH2 CH2 CH2CH3 + CH3 CH2 Cu + LiCl
Ethyl Group
Propyl Group

Abbreviated:

Alternative Last Step:

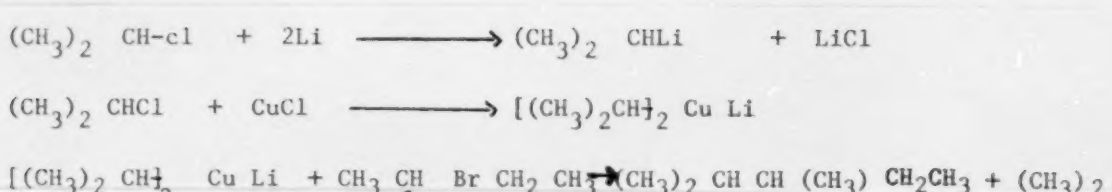


Abbreviated:

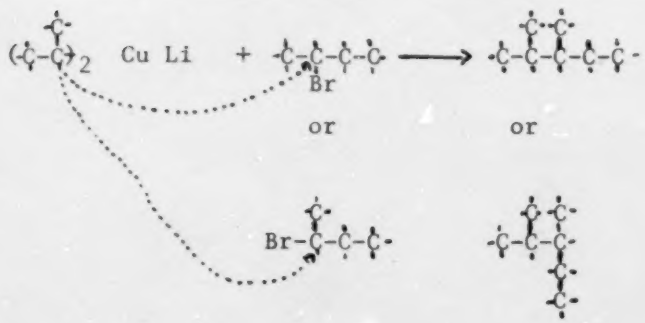


SIP #5 - Tape 1 Worksheet

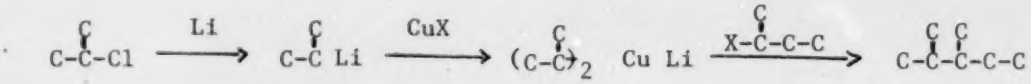
Example 7.



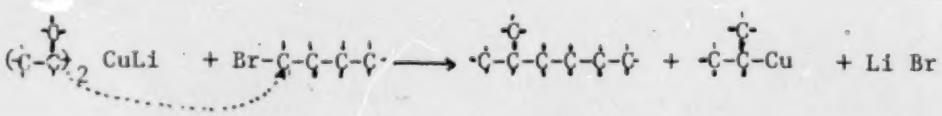
Or



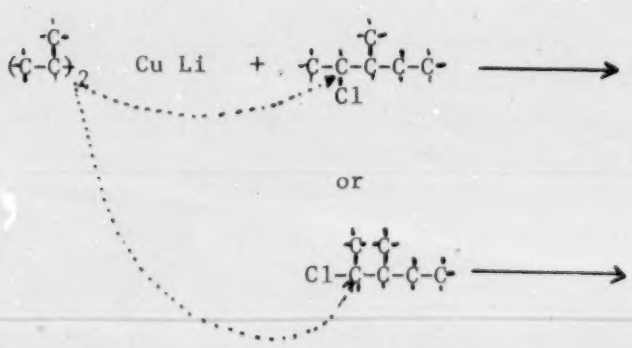
Abbreviated:



Alternate Last Step.



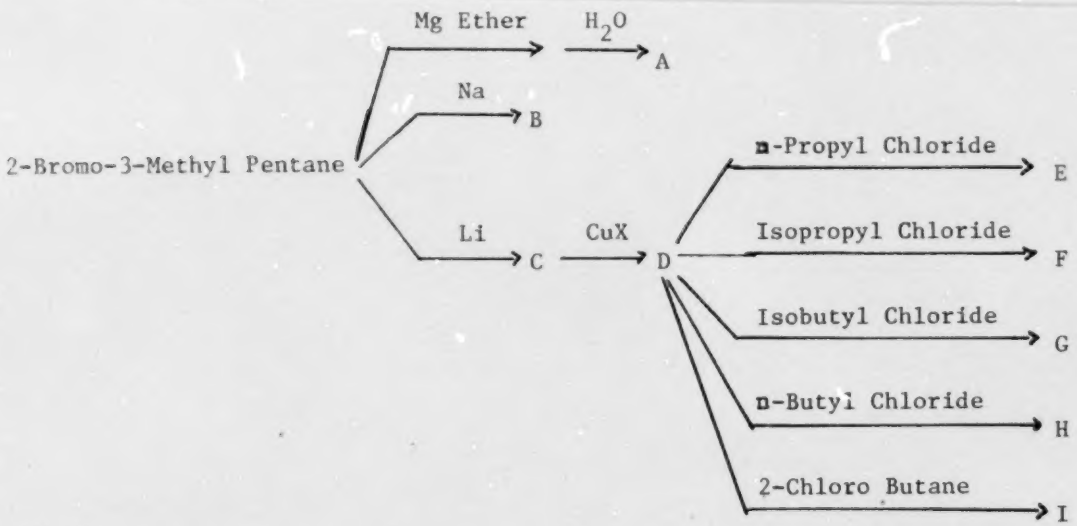
Alternate Last Step.



SIP #5 - Tape 1 Worksheet

Assignment No. 11

Draw the structures and name compounds A through I in the reactions below. The reactions are given in the abbreviated form. (This should in no way prevent you from writing the balanced equations involved.)



Assignment No. 12

Identify the reagents in the following laboratory synthesis:

a. 2-Bromo Butane → 2,4-Dimethyl Hexane
2-Bromo Butane → 3,4-Dimethyl Hexane

b. 2-Chloro-3-Ethyl Pentane → 2,4-Dimethyl-5-Ethyl Heptane
2-Chloro-3-Ethyl Pentane → 4-Methyl-3-Ethyl-Heptane

Assignment No. 12 (continued)

c. 3-Chloro Pentane → 3,4-Diethyl Hexane
→ 2,3-Dimethyl-4-Ethyl Hexane

Assignment No. 13

Confused Clyde was asked to identify the reactants in a number of laboratory synthesis. He listed all the reactants below but failed to identify them with the synthesis above. It is your task to select the correct reactant for each synthesis.

$\xrightarrow{Na}$ 3,6-Dimethyl-4,5-Diethyl Octane

$\xrightarrow{Mg\ Ether}$ $\xrightarrow{H_2O}$ 3-Methyl-4-Ethyl Heptane

$\xrightarrow{Li}$ $\xrightarrow{CuBr}$ 1-Bromo-3-Methyl Pentane $\longrightarrow$ 3,3,6-Trimethyl Octane

$\xrightarrow{Li}$ $\xrightarrow{CuCl}$ Isobutyl Chloride $\longrightarrow$ 2,3,3,6-Tetramethyl Heptane

$\xrightarrow{Li}$ $\xrightarrow{CuCl}$ n-Propyl Chloride $\longrightarrow$ 2,3,3,6-Tetramethyl Nonane

Reactants:
A. 1-Chloro-2,2,3-Trimethyl Butane
B. 2-Bromo-3-Methyl-4-Ethyl Heptane
C. 3-Chloro-4-Methyl Hexane
D. 2-Chloro-5,5,6-Trimethyl Heptane
E. 2-Bromo-2-Methyl Butane

SIP #5 - Tape 1 - Worksheet

Assignment No. 14

Write all the steps in the laboratory synthesis of the following compounds.

a. 2-Methyl Pentane from Propane

b. 3-Methyl 4-Ethyl Hexane from Butane

c. 2,2,4-Trimethyl Pentane from Isobutane

d. 3,4-Dimethyl Hexane from Butane

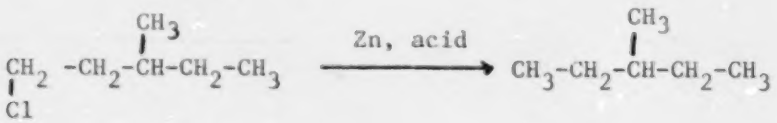
Self Instructional Package No. 5
Tape 1 - Answer Sheet

ALKANES - PREPARATION

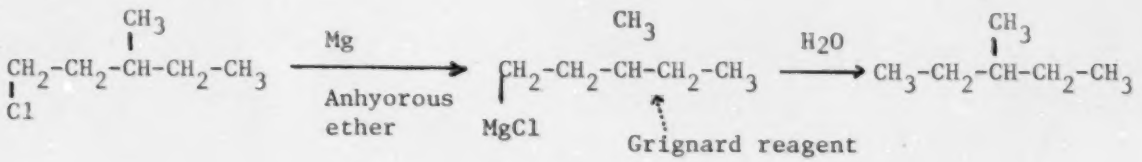
Assignment No. 1

There are two ways to prepare an alkane from an alkyl halide with the SAME (identical) carbon skeleton.

I. Reduction with Zn and acid



II. Grignard Preparation



Assignment No. 2

I. Reduction with Zn and acid

Incorrect:
$(CH_3CH\ (CH_3)\ CH_2\ Br \xrightarrow{Zn} CH_3\ CH(CH_3)_2)$ Zinc without acid will give no reaction

Correct:
$CH_3CH(CH_3)\ CH_2\ Br \xrightarrow{Zn,\ acid} CH_3\ CH\ (CH_3)_2$

II. Grignard Reaction

Incorrect:
$(CH_3\ CH\ (CH_3)\ CH_2\ Br \xrightarrow{H_2O} \xrightarrow{Mg,\ ether} CH_3\ CH\ (CH_3)_2)$

An alkyl halide must react with Mg in ether FIRST and then in the second step the GRIGNARD compound reacts with water to yield the alkane.

Correct:
$CH_3\ CH(CH_3)CH_2\ Br \xrightarrow{Mg\ ether} CH_3CH\ (CH_3)CH_2\ MgBr \xrightarrow{H_2O} CH_3CH(CH_3)_2$

Or:
$CH_3\ CH\ (CH_3)\ CH_2\ Br \xrightarrow{Mg\ ether} \xrightarrow{H_2O} CH_3\ CH\ (CH_3)_2$

SIP No. 5
Tape 1 - Answer Shee.

Assignment No. 3

2-Bromo Butane —Na (Wurtz Synthesis)→ 3,4-Dimethyl Hexane

2-Bromo Butane —Zn, Acid / or / Mg, Ether then H_2O→ Butane

1-Chloro-2-Methyl Butane —Na→ 3,6-Dimethyl Octane

Assignment No. 4

a. (Isopropyl Bromide —Zn, Acid→ Propane)

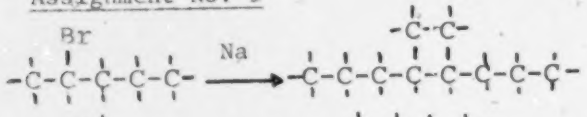
Correct:
1-Chloro-2,3-Dimethyl Butane —Zn, Acid→ 2,3-Dimethyl Butane

b. (2-Bromo Butane —Na→ 2,3-Dimethyl Butane)

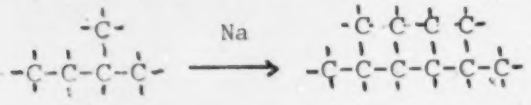
2-Bromo Propane —Na→ 2,3-Dimethyl Butane

c. 2-Bromo Butane —Mg, Ether then H_2O→ Butane correct

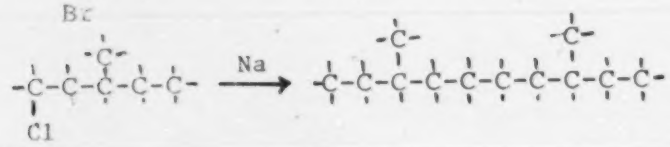
Assignment No. 5



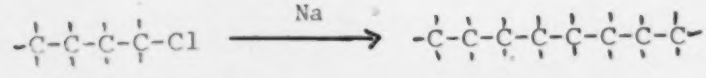
4,5-Dimethyl Octane



2,3,4,5-Tetramethyl Hexane



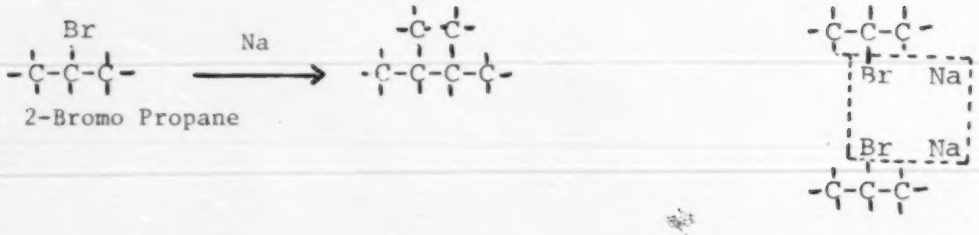
3,8-Dimethyl Decane



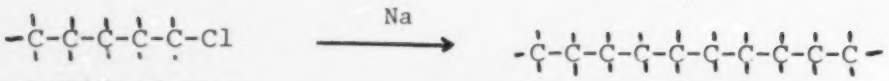
Octane

SIP No. 5
Tape 1 - Answer Sheet

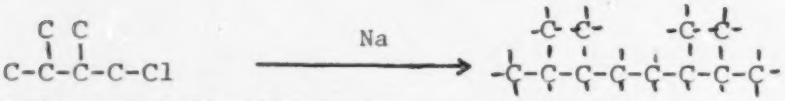
Assignment No. 6



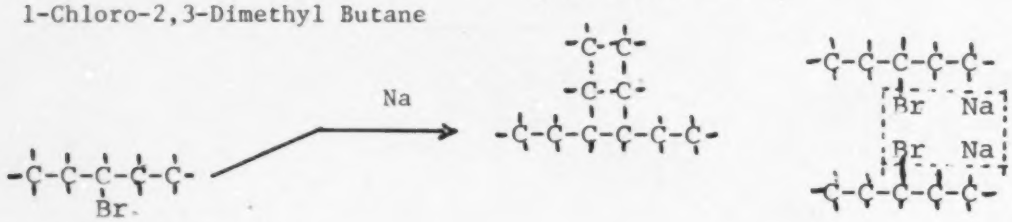
2-Bromo Propane



1-Chloro Pentane



1-Chloro-2,3-Dimethyl Butane



3-Bromo Pentane

Assignment No. 7

1-Bromo-4-Methyl Hexane $\xrightarrow{Zn,\ Acid}$ (4) 3-Methyl Hexane

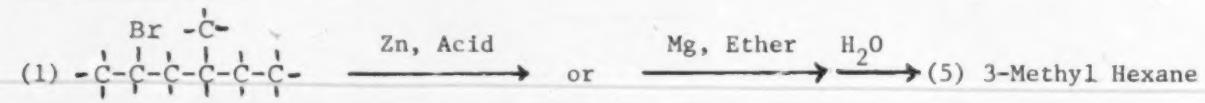
2-Bromo Hexane $\xrightarrow{Na}$ (5) 5,6-Dimethyl Decane

3-Bromo Hexane $\xrightarrow{Na}$ (2) 4,5-Diethyl Octane

2-Bromo-3-Methyl Pentane $\xrightarrow{Na}$ (1) 3,4,5,6-Tetramethyl Octane

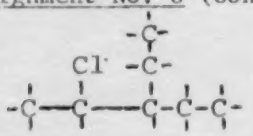
3-Chloro-2-Methyl Pentane $\xrightarrow{Mg,\ Ether}$ $\xrightarrow{H_2O}$ 2-Methyl Pentane

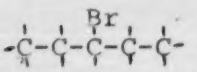
Assignment No. 8

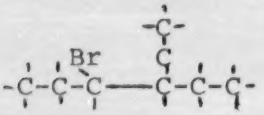


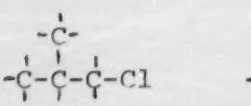
SIP No. 5
Tape 1 - Answer Sheet

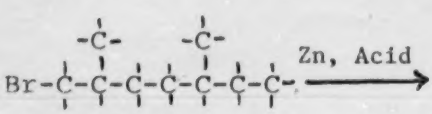
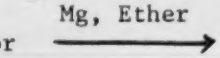
Assignment No. 8 (Continued)

(2)  (4) 4,5-Dimethyl-3,6-Diethyl Octane

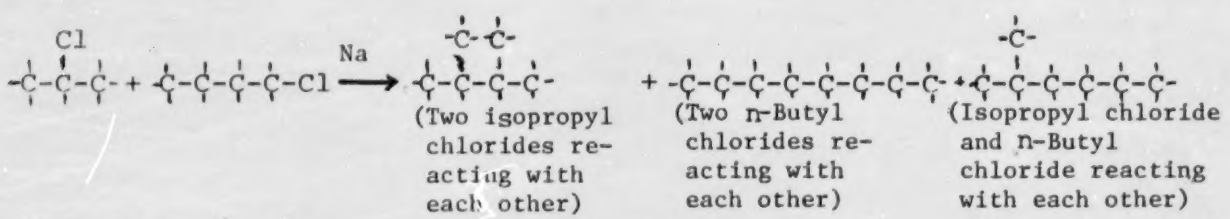
(3)  (1) 3,4-Diethyl Hexane

(4)  or (6) 3-Ethyl Hexane

(5)  (2) 2,5-Dimethyl Hexane

(6)  or  (3) 2,5-Dimethyl Heptane

Assignment No. 9



(Two isopropyl chlorides reacting with each other)

(Two n-Butyl chlorides reacting with each other)

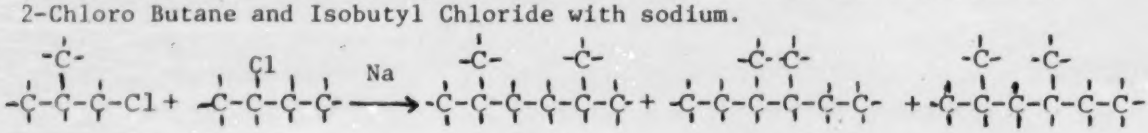
(Isopropyl chloride and n-Butyl chloride reacting with each other)

Assignment No. 10

3,4-Dimethyl Hexane is symmetrical and results from the reaction of 2-Chloro Butane with sodium.

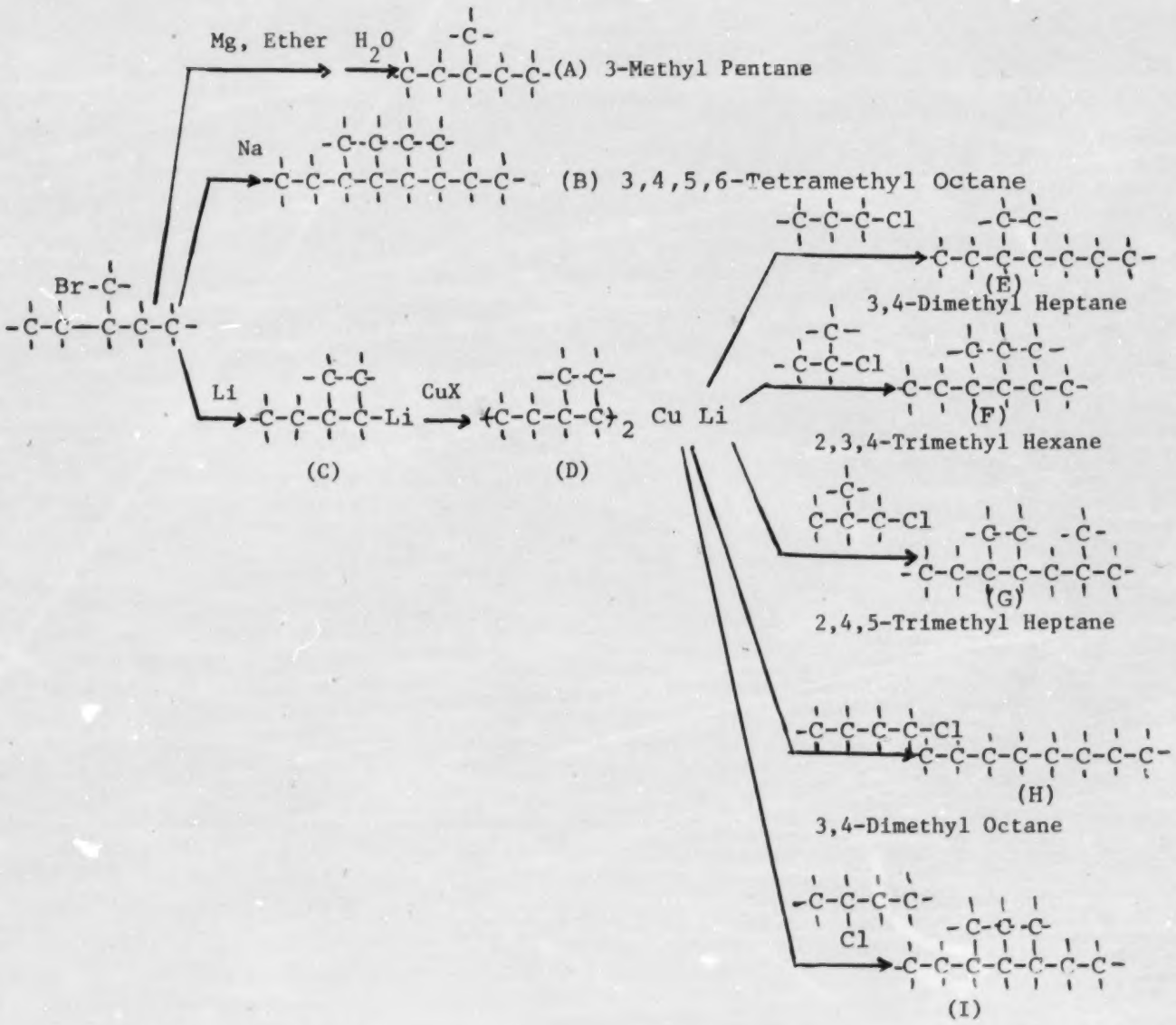
2,5-Dimethyl Hexane is symmetrical and results from the reaction of Isobutyl Chloride with sodium.

2,4-Dimethyl Hexane is NOT symmetrical and results from the reaction of:
2-Chloro Butane and Isobutyl Chloride with sodium.



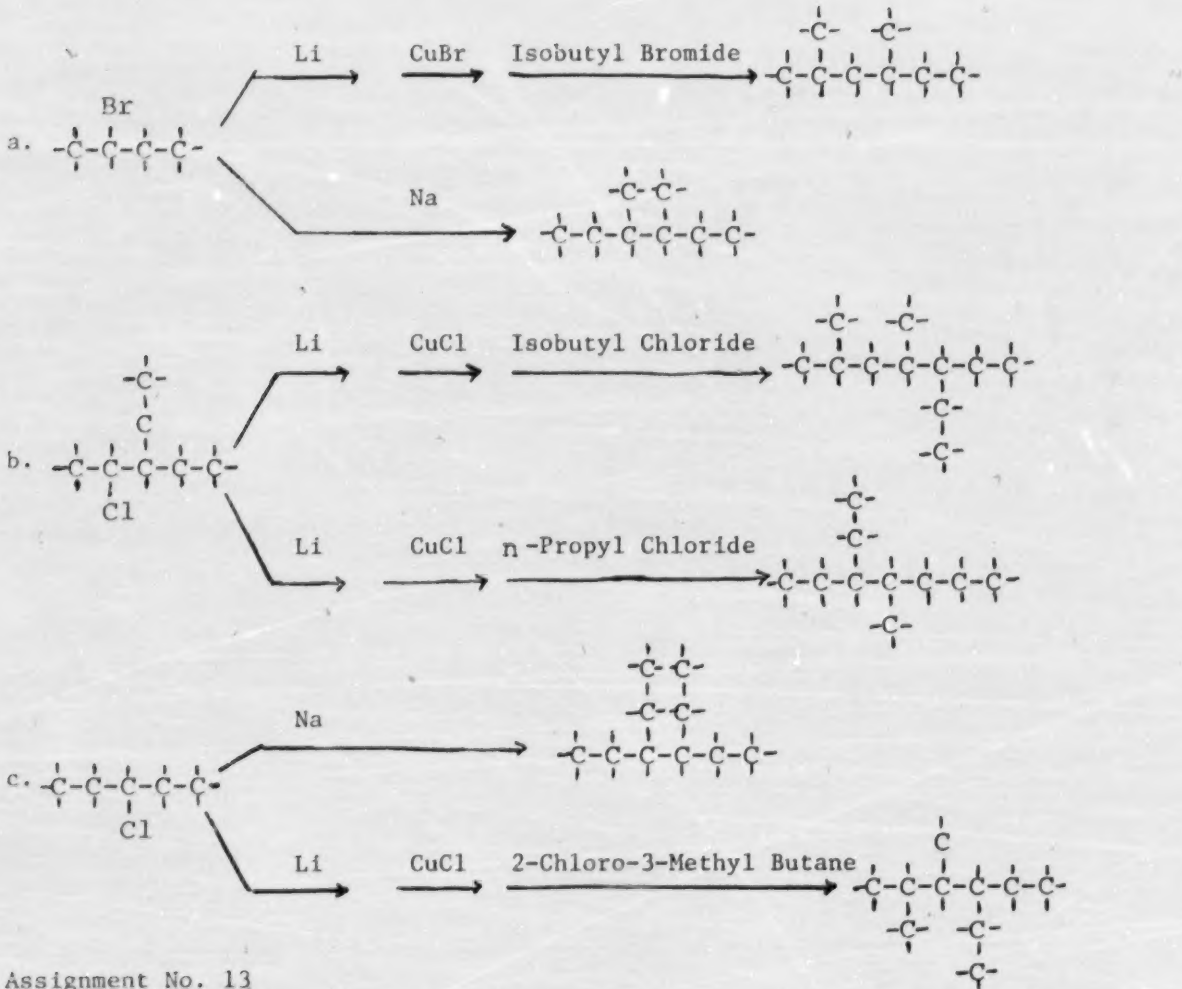
SIP No. 5
Tape 1 - Answer Sheet

Assignment No. 11

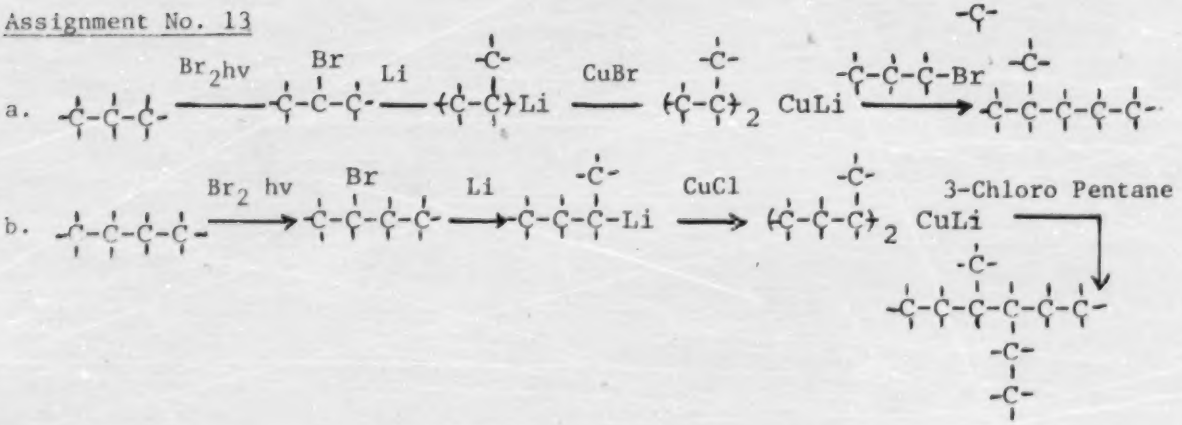


SIP No. 5
Tape 1 - Answer Sheet

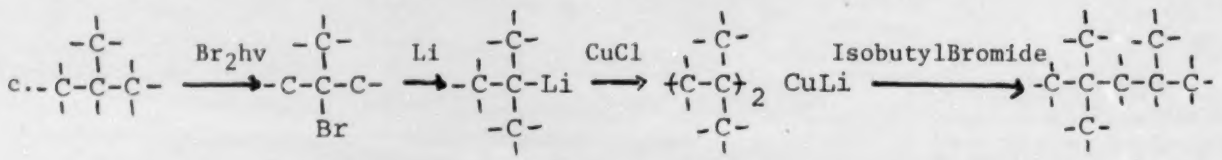
Assignment No. 12

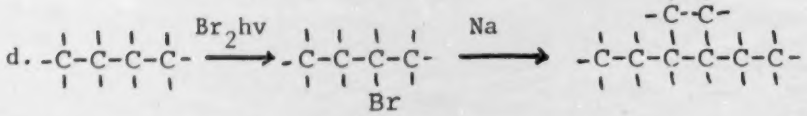


Assignment No. 13



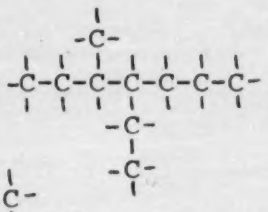
Assignment No. 13 (continued

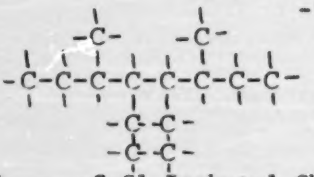
c. 

d. 

Assignment No. 14

a. 1-Chloro-2,2,3-Trimethyl Butane —Li→ —CuCl→ —Isobutyl Chloride→ 2,3,3,6-Tetramethyl Heptane

b. 2-Bromo-3-Methyl-4-Ethyl Heptane —Mg, Ether→ —H_2O→ 

c. 3-Chloro-4-Methyl Hexane —Na→ 

d. 2-Chloro-5,5,6-Trimethyl Heptane —Li→ —CuCl Isobutyl Chloride→ 2,3,3,6-Tetramethyl Nonane

e. 2-Bromo-2-Methyl Butane —Li→ —CuBr→ —1-Bromo-3-Methyl Pentane→ 3,3,6-Trimethyl Octane

What is not fully
understood is not
possessed.--Goethe

Self Instructional Package No. 5
Tape 2 - Worksheet

ALKANES - REACTIONS

Parum Affinis - Without Affinity

I. Halogenation Reaction

$$C_nH_{2n+2} + X_2 \xrightarrow{\text{Heat or Light}} C_nH_{2n+1}X + HX$$

II. Combustion Reaction

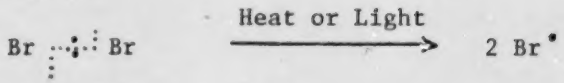
$$C_nH_{2n+2} + \text{Excess } O_2 \xrightarrow{\text{Heat}} nCO_2 + (n+1)\ H_2O$$

Assignment No. 1

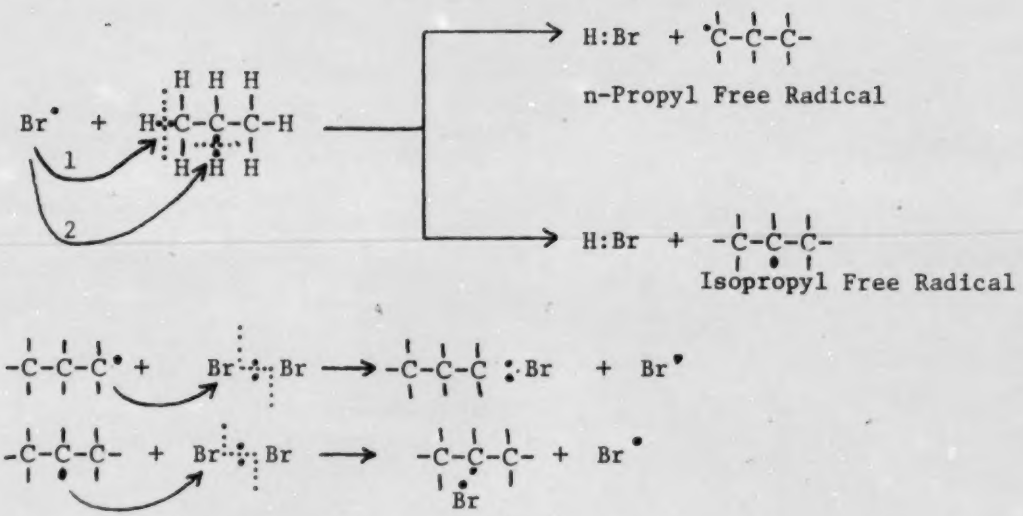
Write the step by step mechanism for the bromination of Ethane.

Example No. 1

Chain Initiating Step:



Chain Propagating Steps:

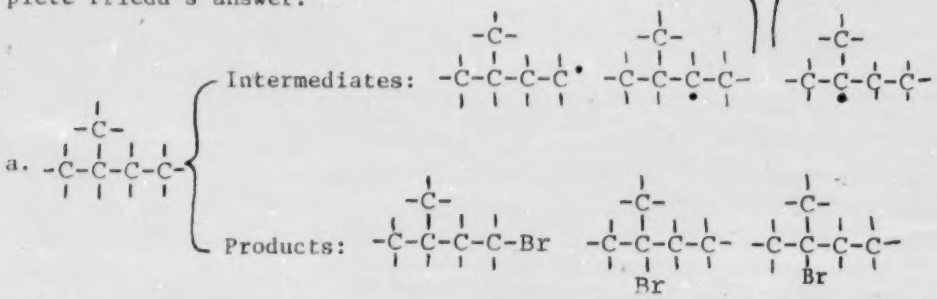


Assignment No. 2

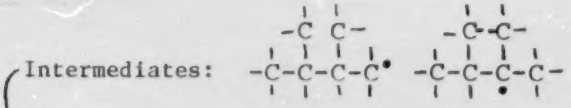
Write the step by step mechanism for the bromination of: Isobutane and 2-Methyl Pentane. Identify (draw the structure and name) all the possible intermediate free radicals and all the products.

Assignment No. 3

Forgetful Frieda was asked to identify all the intermediates and all the products in a number of reactions. Her answer is given below. In many answers she has forgotten something. Complete Frieda's answer.

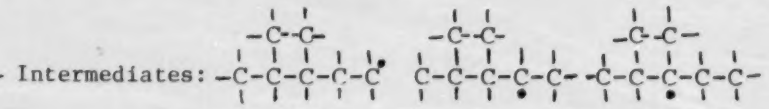
a. 

b. 2,3-Dimethyl Butane



Products: 1-Bromo-2,3-Dimethyl Butane
2-Bromo-2,3-Dimethyl Butane

c. 2,3-Dimethyl Pentane



Products: 1-Bromo-3,4-Dimethyl Pentane
2-Bromo-3,4-Dimethyl Pentane
3-Bromo-2,3-Dimethyl Pentane

Assignment No. 4

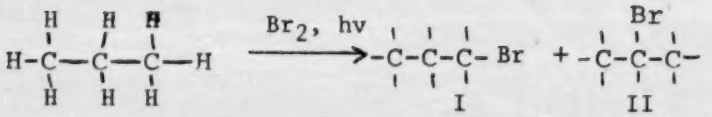
A number of monohalogenated products are listed below. Identify (Draw the structure and name) the reactant for each group of products.

a. 1-Bromo-3-Methyl Pentane 2-Bromo-3-Methyl Pentane 3-Bromo-3-Methyl Pentane

b. 1-Bromo-3,4-Dimethyl Hexane 2-Bromo-3,4-Dimethyl Hexane 3-Bromo-3,4-dimethyl hexane

c. 1-Bromo-3-Ethyl Pentane 2-Bromo-3-Ethyl Pentane 3-Bromo-3-Ethyl Pentane

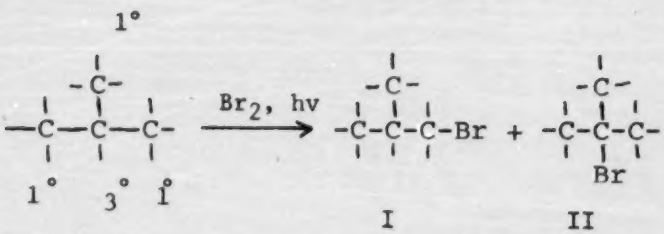
Example No. 2



1° 2° 1°

Expected Ratio	Observed %
I : II	I : II
3 : 1	3% 97%
	or
	1 : 32 Ratio

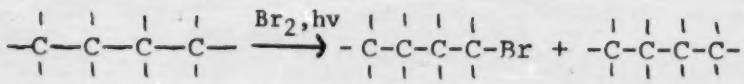
Ratio: 1°/2° = 6/2 = 3/1



1° 3° 1°

9 : 1 ~0 : 99%

Ratio: 1°/2° = 9/1



1° 2° 2° 1°

3 : 2 2% : 98%

or

1 : 49 Ratio

Ratio: 1°/2° = 6/4 = 3/2

Example No. 3

Rate of Reaction = Total No. of Collisions per cc per sec. X Fraction of Collisions that have sufficient energy X Fraction of Collisions that have proper orientation

Rate = Collision Frequency X Probability Factor X Energy Factor

Example No. 3 (continued)

E act for the abstraction of $2^{\circ}H \neq$ E act for the abstraction of $1^{\circ}H$

$$E_{act\ 2^{\circ}} \gtrless E_{act\ 1^{\circ}}$$

$$E_{act\ 3^{\circ}} < E_{act\ 2^{\circ}} > E_{act\ 1^{\circ}}$$

RATE OF ABSTRACTION OF H ATOMS: $3^{\circ} > 2^{\circ} > 1^{\circ}$

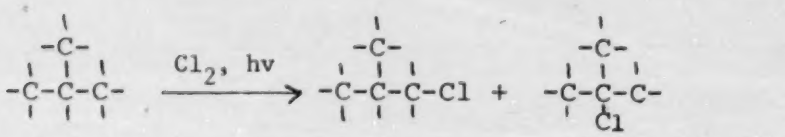
EASE OF ABSTRACTION OF H ATOMS: $3^{\circ} > 2^{\circ} > 1^{\circ}$

Example No. 4

Chlorination Reaction

Relative rates of reaction per hydrogen atom: 5.0 : 3.8: : 1.0

(3° : 2° 1°)



Isobutane — Isobutyl Chloride — t-Butyl Chloride

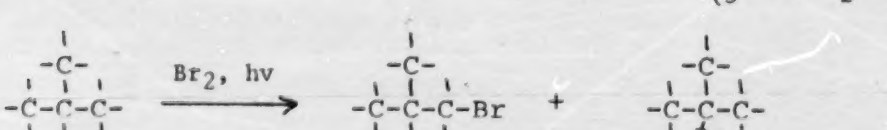
$$\frac{\text{Isobutyl Chloride}}{\text{tert Butyl Chloride}} = \frac{\text{No. of } 1^{\circ}H}{\text{No. of } 3^{\circ}H} \times \frac{\text{Reactivity of } 1^{\circ}H}{\text{Reactivity of } 3^{\circ}H} = \frac{9}{3} \times \frac{1.0}{5.0} \quad \frac{9}{15}$$

$\frac{9}{15}$ $\frac{35.7\%}{64.3\%}$ $(\frac{9}{26} \times 100)$ $(\frac{15}{26} \times 100)$

Bromination Reaction

Relative rates of reaction per hydrogen atom: 1600 : 82 : 1

(3° 2° 1°)



Isobutane — Isobutyl Bromide — t-Butyl Bromide

Example No. 4 (continued)

Isobutyl Bromide	No. of 1°H	Reactivity of 1°H	9 x 1		1
t-Butyl Bromide	No. of 3°H	Reactivity of 3°H	1 x 1600	1600	178

Exclusively t-Butyl Bromide

Assignment No. 5

Calculate the percentage composition of the products obtained from: a.) Chlorination and b.) Bromination of Propane and Butane. Compare these results to those obtained experimentally. (You can find them in Example No. 7)

Assignment No. 6

Identify - draw structure and name the MAJOR product in the reactions written below.

3,4-Dimethyl Hexane $\xrightarrow{Br_2,\ hv}$

2,2-Dimethyl Propane $\xrightarrow{Cl_2,\ hv}$

2-Methyl Pentane $\xrightarrow{Br_2,\ hv}$

3-Ethyl Pentane $\xrightarrow{Br_2,\ hv}$

Table I

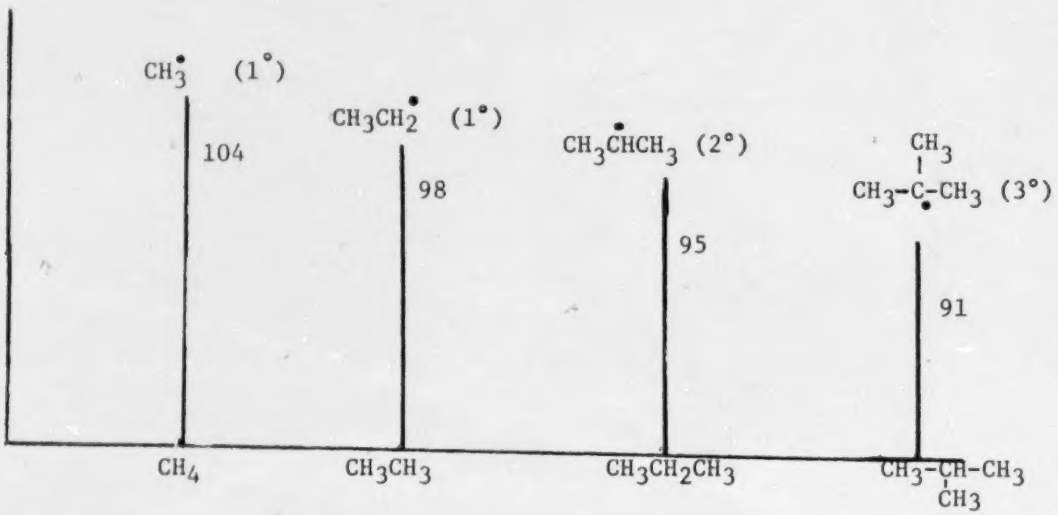
Energies of Reactivation [$\frac{\text{Kcal}}{\text{Mole}}$] for the Reaction: $R{\cdot\cdot}H + X^{\bullet} \longrightarrow R^{\bullet} + H{\cdot\cdot}X$

R	X = Cl	X = Br
CH_3	4	18
1°	1	13
2°	0.5	10
3°	0.1	7.5

Example No. 5

EASE OF FORMATION OF FREE RADICALS: 3° > 2° > 1° > $CH_3^{\bullet}$

Example No. 6

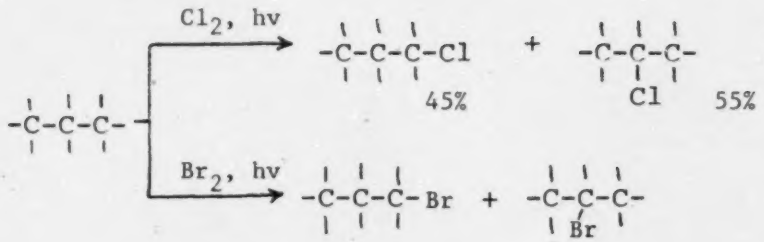


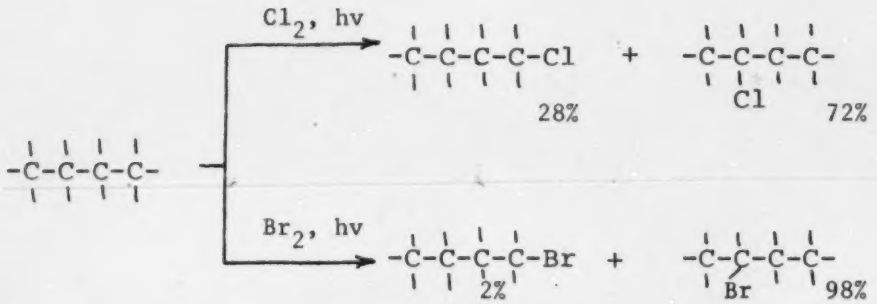
STABILITY OF FREE RADICALS: 3° > 2° > 1° > $CH_3^{\bullet}$

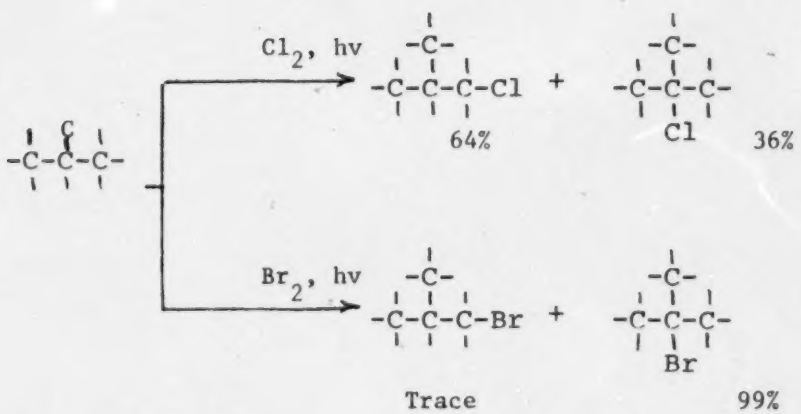
ORIENTATION - where in the given molecule the reaction will take place predominately - comparison of different sites of the SAME MOLECULE.

REACTIVITY - Comparison of Different Compounds in a reaction with the same reagent.

Example No. 7

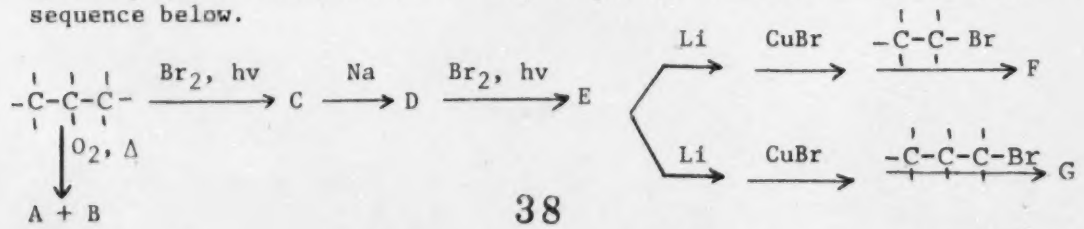






Assignment No. 7

Identify (draw structures and name) compounds A → G in the reaction sequence below.



Assignment No. 8

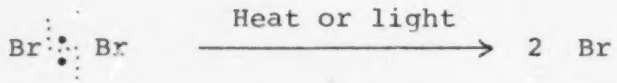
Write all the steps in the laboratory synthesis of 3-Methyl Pentane from n-propyl chloride.

Self Instruction Package No. 5
Tape 2 - Answer Sheet

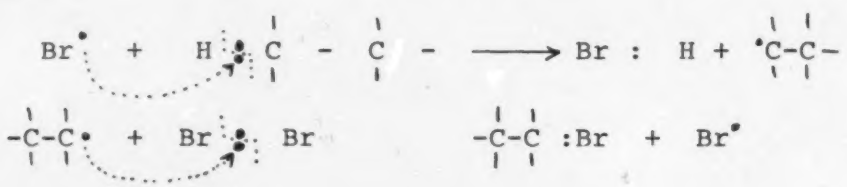
ALKANES - REACTIONS

Assignment No. 1

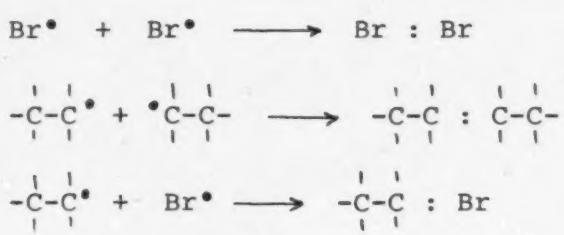
Chain Initiating Step



Chain Propagating Steps

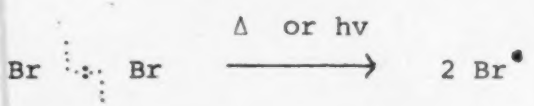


Chain Terminating Steps



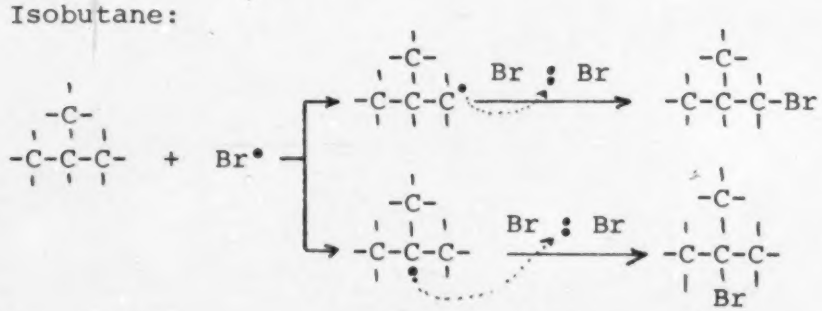
Assignment No. 2

Chain Initiating Step



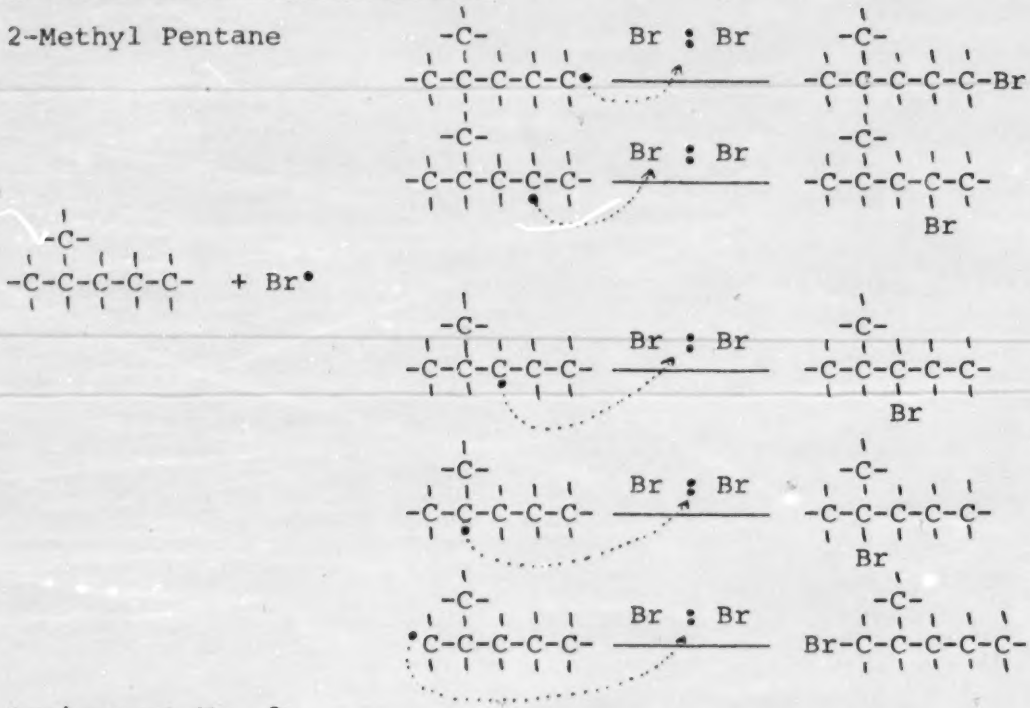
Chain Propagating Steps

Isobutane:

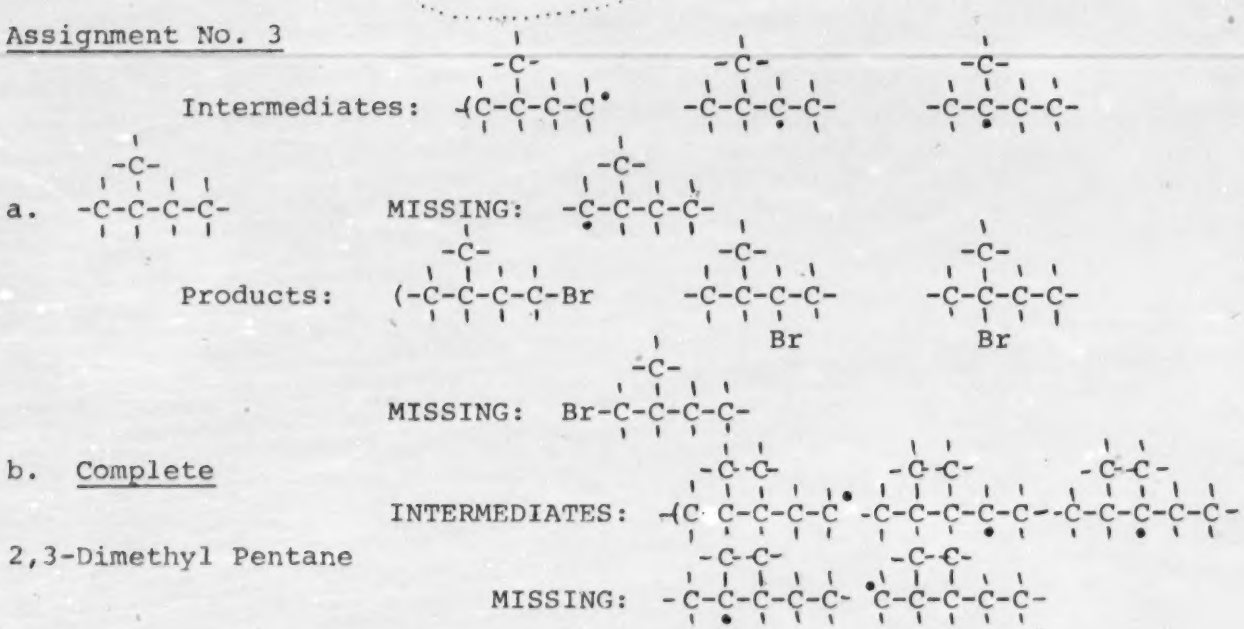


Assignment No. 2 (continued)

2-Methyl Pentane



Assignment No. 3

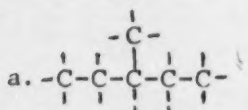


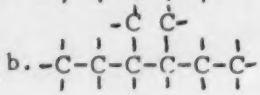
b. Complete

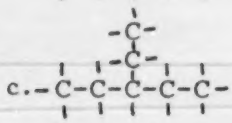
2,3-Dimethyl Pentane

PRODUCTS: 1-Bromo-3,4-Dimethyl Pentane
2-Bromo-3,4-Dimethyl Pentane
3-Bromo-2,3-Dimethyl Pentane
2-Bromo-2,3-Dimethyl Pentane
1-Bromo-2,3-Dimethyl Pentane

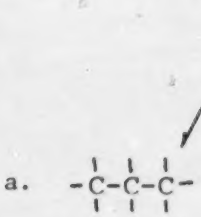
Assignment No. 4

a.  3-Methyl Pentane

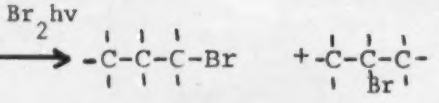
b.  3,4-Dimethyl Hexane

c.  3-Ethyl Pentane

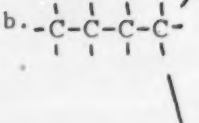
Assignment No. 5

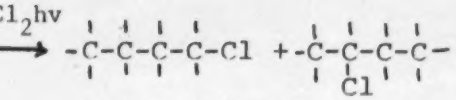
a. 

$$\frac{\text{n-Propyl Chloride}}{\text{Isopropyl Chloride}} = \frac{6 \times 1}{2 \times 3.8} = \frac{6}{7.6} = \frac{1}{1.27} = \frac{44.1\%}{55.9\%} \quad \frac{\left(\frac{6}{13.6} \times 100\right)}{\left(\frac{7.6}{13.6} \times 100\right)}$$

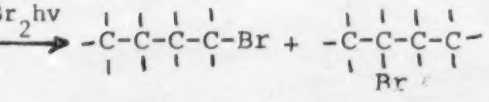


$$\frac{\text{n-Propyl Bromide}}{\text{Isopropyl Bromide}} \quad \frac{6 \times 1}{2 \times 82} = \frac{6}{164} = \frac{1}{27.3} = \frac{44.1\%}{55.9\%} \quad \frac{\left(\frac{6}{170} \times 100\right)}{\left(\frac{6}{170} \times 100\right)}$$

b. 

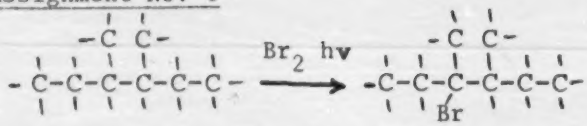


$$\frac{\text{n-Butyl Chloride}}{\text{Sec. Butyl Chloride}} = \frac{6x1}{4 \times 3.8} = \frac{6}{15.2} = \frac{28.3\%}{71.7} \quad \frac{\left(\frac{6}{21.2} \times 100\right)}{\left(\frac{15.2}{21.2} \times 100\right)}$$

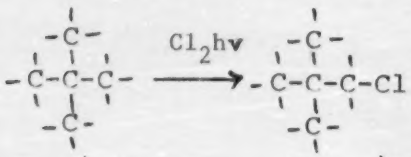


$$\frac{\text{m-Butyle Bromide}}{\text{Sec. Butyl Bromide}} = \frac{6x1}{4x82} = \frac{6}{328} = \frac{1.8\%}{98.2\%} \quad \frac{\left(\frac{6}{334} \times 100\right)}{\left(\frac{328}{334} \times 100\right)}$$

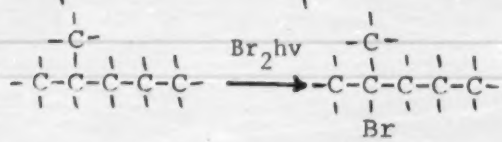
Assignment No. 6



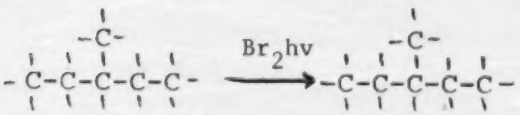
3-Bromo-3,4-Dimethyl Hexane



1-Chloro-2,2-Dimethyl Propane

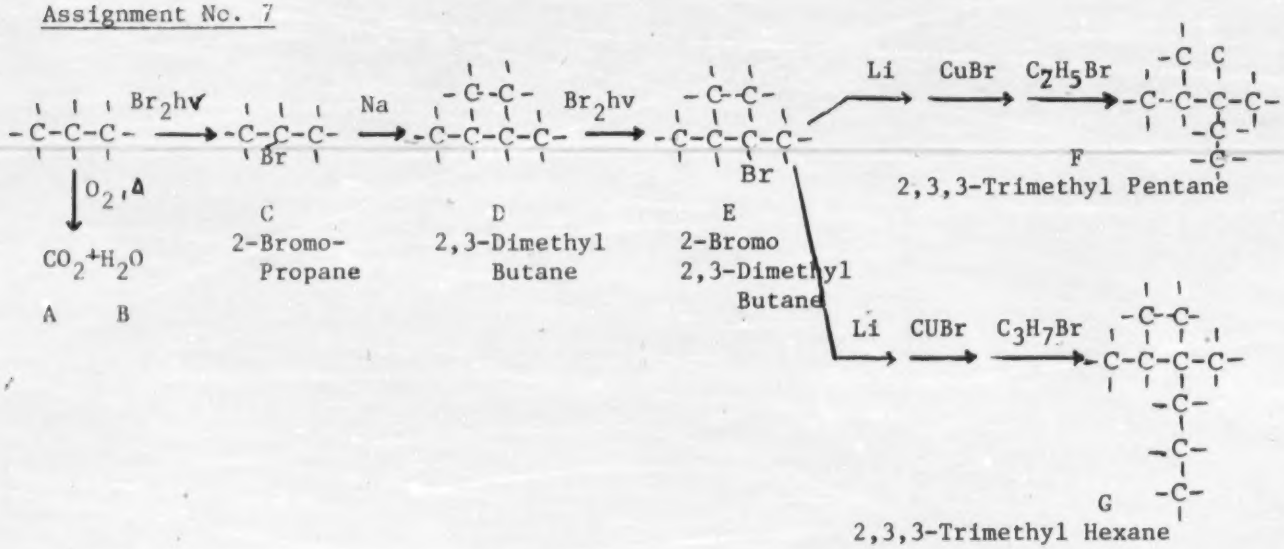


2-Bromo-2-Methyl Pentane

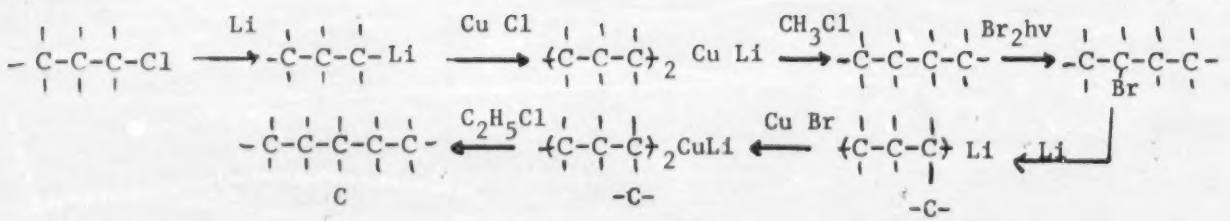


3-Bromo-3-Methyl Pentane

Assignment No. 7



Assignment No. 8



Self Instructional Package No. 5
Form D - Progress Check Evaluation

ALKANES - PREPARATION AND REACTIONS

1. When butane reacts with excess oxygen in the present of heat the products will be:

   a) carbon dioxide

   b) carbon dioxide and water

   c) heat and carbon monoxide

   d) carbon dioxide, water and heat.

2. Hydrocracking of alkanes can be defined as:

   a) the reaction of an alkane with excess oxygen.

   b) the reaction of alkanes in which smaller alkanes are produced.

   c) the decomposition of alkanes with heat in presence of hydrogen.

   d) the decomposition of alkanes with heat in presence of steam.

3. The following statements about the pyrolysis are true:

   a) the pyrolysis of alkanes is known as cracking.

   b) the pyrolysis is the decomposition of a compound.

   c) the pyrolysis is the decomposition of a compound by the action of heat.

   d) the pyrolysis is the decomposition of a compound in the presence of steam.

4. The most and the least stable free radical in the series of free radicals:

   $CH_3\text{-}\overset{\bullet}{C}H\text{-}CH_3$ $\quad CH_3\overset{\bullet}{C}H_2$ $\quad CH_3\text{-}\overset{CH_3}{\overset{|}{\underset{\bullet}{C}}}\text{-}CH_3$ $\quad CH_3\text{-}\overset{CH_3}{\overset{|}{C}}H\text{-}\overset{\bullet}{C}H_2$

   are:

The most stable free radical	The least stable free radical
a) Ethyl	a) Isobutyl
b) T-Butyl	b) Ethyl
c) Isobutyl	c) Isopropyl
d) Ethyl	d) T-Butyl

5. In each pair of alkanes, identify the one which is more reactive toward halogenation reaction:

	More Reactive
a) Methane(A), Ethane (B)	_____
b) Propane(A), Isobutane (B)	_____
c) Isobutane(A), Butane (B)	_____
d) Ethane (A), Propane (B)	_____

6. The laboratory preparation of 3,4-dimethyl hexane from butane can be achieved by the use of the following reagents:

   a) BROMINE, light, SODIUM

   b) BROMINE, Light, MAGNESIUM IN ETHER, WATER

   c) SODIUM

   d) BROMINE, Light, LITHIUM, COPPER BROMIDE, 2-BROMO BUTANE

7. The reactant required for the Grignard synthesis is:

   a) an alkane

   b) an alkyl bromide

   c) an alkyl chloride

   d) an alcohol.

8. Identify the correct statements below:

   a) Tertiary alkyl halides give best results in Wurtz synthesis.

   b) Primary alkyl halides give best results in the reaction with Lithium Dialkyl Copper Intermediate.

   c) Grignard synthesis is a one-step preparation.

   d) A Grignard compound can react with water or ammonia or alcohols to produce an alkane.

9. The reagents required to convert 2-Chloro Butane into 3-Methyl Pentane are:

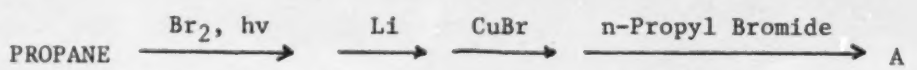
   a) SODIUM

   b) MAGNESIUM IN ETHER, WATER

   c) LITHIUM, COPPER CHLORIDE, ETHYL CHLORIDE

   d) LITHIUM, COPPER, CHLORIDE, PROPYL CHLORIDE

10. The product A obtained in the reaction sequence below is:



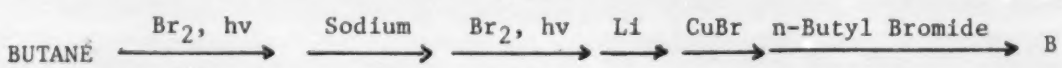
   a) Hexane

   b) 3-Methyl Pentane

   c) 2-Methyl Pentane

   d) 2-Methyl Hexane

11. The compound B produced in the reaction below is:



   a) 4-n-Butyl Octane

   b) 3,4-Dimethyl-4-Ethyl Octane

   c) 3,4,4-Trimethyl Nonane

   d) Dodecane

12. The major product in the Bromination of 2-Methyl Butane is:

    a) 1-Bromo-2-Methyl Butane

    b) 2-Bromo-2-Methyl Butane

    c) 2-Bromo-3-Methyl Butane

    d) 1-Bromo-3-Methyl Butane

13. The major product in the reaction of 2-Bromo Butane with Zinc in presence of Acid is:

    a) 3,4-Dimethyl Hexane

    b) Octane

    c) Butane

    d) Organozinc Compound

Self Instructional Package No. 5

Form B^1 - Answer Sheet

ALKANES - PREPARATIONS AND REACTIONS

1. b, d
2. a, b, c
3. a, b
4. c
5. b, c
6. c
7. a
8. b
9. d
10. a, c
11. d
12. d
13. a, b
14. a, b
15. a, b

Self Instructional Package No. 5

Form D^1 - Answer Sheet

ALKANES - PREPARATIONS AND REACTIONS

1. d
2. c
3. a, c
4. b
5. B, B, A, A
6. a, d
7. b, c
8. b, d
9. c
10. c
11. b
12. b
13. c

CHEM 201

S.I.P. #5 - ERRATA

FORM B - Question #7 - Reaction:

2-Methyl Butane $\xrightarrow{Br_2,h\nu}$ $\xrightarrow{Na}$ $\xrightarrow{Br_2,h\nu}$ $\xrightarrow{Li}$ $\xrightarrow{CuBr}$ $\xrightarrow{\text{Ethyl Bromide}}$ B

Question #11 - Reaction:

A $\xrightarrow{Br_2,h\nu}$ $\xrightarrow{Li}$ $\xrightarrow{CuBr}$ $\xrightarrow{\text{2-Bromo Butane}}$ 2,3-Dimethyl Pentane

Question #14 - Part a.

a) Hydrocracking is the cracking of alkanes in the presence of hydrogen

FORM D[1] - Answer Sheet

5 - B. B. A. B

TAPE 1 - Answer Sheet

The answers for assignments 13 and 14 are reversed. (The answer listed for assignment 13 is actually the answer for assignment 14.)

TAPE 2 - Worksheet - Example No. 4

$$\frac{\text{Isobutyl Chloride}}{\text{Tert. Butyl Chloride}} = \frac{\text{No. of } 1^\circ H}{\text{No. of } 3^\circ H} \times \frac{\text{Reactivity of } 1^\circ H}{\text{Reactivity of } 3^\circ H} = \frac{9 \times 1.0}{1 \times 5.0} =$$

$$= \frac{9}{5} = \frac{64.3\%}{35.7\%} \quad \left(\frac{9}{14} \times 100\right)$$

$$\left(\frac{5}{14} \times 100\right)$$